

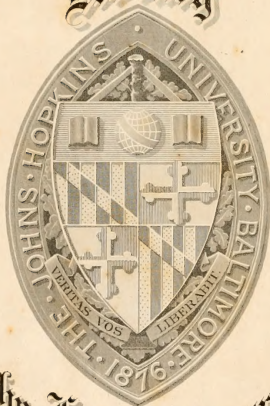
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An Investigation of the  
Composition of Certain  
Oxides of Manganese

A Dissertation  
for the degree of Doctor of  
Philosophy at the  
Johns Hopkins University  
by

Arthur D. Chambers

-1896-

see former  
edition by  
Arthur D.





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### Acknowledgment.

This work was suggested by Professor H. N. Morse and was carried out under his direction. To him the author wishes to express his thanks. He also wishes to acknowledge his indebtedness to Professors Ira Remsen, W. B. Clark, and the late Professor Geo. H. Williams.



## Introduction

The study of the composition of the oxides of manganese which lie between  $Mn_2O_3$  and  $MnO_2$  has attracted the attention of several chemists. A number of the comparatively simple compounds have been described from time to time, among these are  $(2MnO \cdot 3MnO_2)^+$ ,  $(MnO \cdot 2MnO_2)^+$ ,  $(MnO \cdot 4MnO_2)^+$ ,  $(MnO \cdot 5MnO_2)^+$ ,  $(MnO \cdot 11MnO_2)^+$ ,  $(MnO \cdot 23MnO_2)^+$ .

It is also well known that manganese dioxide prepared by wet methods has acid properties and is a soluble salt.

1) Frankel, J. Pr. Chem. 36, 451, 166

2) Reissig, Ann. 103, 77

3) Goren, Bull. Soc. Ch. 57, 1

4) Engen Bull. Soc. Ch. 51, 1

5) Velez Jr. Soc. Ch. 37, 381

6) Velez Jr. Soc. Ch. 37, 381





with many bases, so that if  $MnO_2$  is precipitated in any solution in which salts are present, some of the base will be found in the precipitate.

During the summer of 1900 in this laboratory, the study of the composition of the oxides of manganese which are formed by the decomposition of manganese dioxide, prepared by precipitating manganous sulphate by potassium permanganate, was undertaken by Morse and Walker. Their work had reference only to the manganous oxide; to available oxygen



in these compounds, the values obtained are recorded in Newell's dissertation.

The work herein described is a continuation of that just mentioned, the composition of a number of oxides has been studied not only as regards the ratio of manganous oxide to available oxygen, but also with reference to the amount of water and base which they contain.

Special methods of analysis have been devised and some of the results have been noted in order to show.





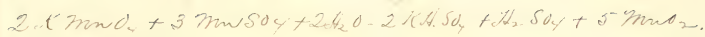
## 1. Preparation of Material

Two different methods were used for the preparation of the manganese dioxide which formed the starting point in the work; in the first it was not attempted to get an oxide entirely free from other bases; in the second, an attempt was made to prepare an oxide free from all bases except  $MnO$ .

Method A. - Manganous sulphate was treated with an excess of potassium permanganate in the presence of nitric acid. The equation representing the reaction



is as following



The actual quantities used were 10 grams of crystallized manganese sulphate, 110 grams of potassium permanganate and 200 grams of 10% nitric acid, the total volume of the mixed solutions amounted to about 2 litres. This made the nitric acid about 10% in strength in the solution, there were about 1 molecule of nitric acid present for every atom of potassium. The precipitation was made at a temperature of about 20°C. by adding the mixed nitric acid and manganese



sulphate solutions is to that of the permanganate, so that at all times there was an excess of the permanganate.

The oxide was washed first by maceration, then by filtration on an asbestos filter and washed until free from impurities soluble in water. The ratio of MnO to oxygen was then determined and found to correspond to the formula  $MnO_{1.2}$ .

This is essentially the method employed by Morse and Walker in the preparation of the oxides used by them.

Method B. The essential difference





between This and the method  
given above is that ammonium  
permanganate was used  
instead of the potassium salt.  
The ammonium permanganate  
was prepared as follows:  
Concentrated solutions of  
potassium permanganate  
and silver nitrate were mixed,  
the precipitated silver salt  
was filtered off, and twice  
recrystallized from water,  
the oxides which formed  
on heating being removed  
each time by filtering  
through asbestos. The silver  
salt was then ground  
in a large mortar  
with an equivalent



amount of ammonium  
bromide, sufficient water  
being added to dissolve  
the ammonium permanganate.  
It cannot be prepared by  
mixing together hot solutions  
of the two salts on account  
of the ready decomposition  
of the compound. When, however,  
the solution is freed from  
silver bromide and oxides  
of manganese by filtration,  
it can be heated to  $65^{\circ}\text{C}$   
with very little decomposition.

From this solution of ammonium  
permanganate the oxide  
was prepared as directed  
under 4, & was washed  
with dilute nitric acid





until a portion when heated with strong caustic potash solution did not give enough ammonia to be detected by the ~~same~~ <sup>same</sup> litmus paper. It was found however that a quantitative analysis was made that it still contained about 1.5% of ammonia as well as a small amount of silver bromide.

All reagents used in analysis.

1. Potassium permanganate solution. Of this reagent two solutions were used, one of which contained about 3.5 grams per liter. The other about 5 grams per liter.



The weaker solution was used in titrating the excess of tetroxalate in the analyses, and the stronger for the determinations of manganese by the modified Fehling method. The solutions were made from permanganate purified by recrystallization from the commercial salt and were filtered twice through Whatman No. 541, solutions made in this way can be kept for months with scarcely any decrease in strength.

2. A solution of potassium tetroxalate. This contained about 15 grams of the salt per liter. A weaker solution



is not satisfactory for this work on account of <sup>the</sup> length of time it requires to dissolve the residues, especially after they have become very dry. On the other hand, if very little strychnine is used, the chocolate will crystallize out in cold weather.

3. A standard solution of quinine was used, the strength of which was about .25 Normal. It was standardized by weighing the quinine substance, precipitated from measured portions, also by a standard ammoniacal solution according to the method recently described.<sup>1)</sup> The results obtained by the

<sup>1)</sup> Morse and Chambers, Ann. Chem. 18, 236



Two methods showed very close agreement

1. a solution of ammonia.

This was of approximately to N. strength. It was made from a solution which had been freed from carbonate by distilling it from lime. Its relation to the sulphuric acid was determined from time to time.

2. Fine oxide which contains no reducing substances. This was prepared by igniting the commercial oxide for three or four hours in a muffle.

This, when dissolved in sulphuric acid, gave a solution which did not reduce permanganate





6) A. Neutral solution of zinc sulphate which will not reduce permanganate. This is easily prepared by heating a known amount of sulphuric acid with an excess of zinc oxide, prepared as described, until the solution is neutral. The solution is then diluted to a definite volume. A convenient strength is 200 grams to the liter.

7) A neutral solution of hydrogen peroxide. This is prepared by shaking the ordinary solution for some time with zinc oxide. The excess <sup>of the oxide</sup> is removed by filtering through as bestox.



8. Water which is neutral to litmus and contains no reducing substances. This was made from the ordinary distilled water in the following manner. A six-liter flask was connected with a neck of about two and a half liter capacity by a large glass tube which passed through the tubulure and to the bottom of the flask. The neck was directed upwards at an angle of about  $45^\circ$  and was joined by means of an adapter to a Liebig's Condenser. All the openings in the apparatus except the neck of the flask



were closed with asbestos and asbestos paper, as it was found that cork and rubber stoppers were decomposed by the steam and that substances passed over with the water which reduced permanganate.

The flask contained distilled water acidified with sulphuric acid. The retort <sup>and</sup> a strong alkaline solution of potassium permanganate. Both solutions were heated to boiling. The heat was then so regulated that the volume of the solution in the retort remained nearly constant while the steam passed



from the flask through it.  
 A large plug of glass wool  
 in the adapter prevented  
 any carrying over of acids  
 of manganese. Water purified  
 in this way was used in the  
 preparation of reagents  
 and in all the analyses.

#### IV Methods of analysis.

The measuring flasks used were  
 graduated by the method of Morse  
 and Blacklock<sup>1</sup>, the burettes were  
 also calibrated by their method,  
 so that, in the titrations, volumes  
 could be accurately measured  
 to the 100 of a c.c..

A. To determine the ratio of Mn  
 to available O. For this there  
 are required the titration





17  
and permanganate solutions.  
It is not necessary to know their  
absolute strength, <sup>but</sup> only the  
relation between them.

About 2 grams of an oxide  
was placed in a 150 cc. beaker,  
and an excess of the tetroxalate  
measured in, then 50 cc. of  
a 25% solution of sulphuric  
acid were added. The beaker  
was placed in an <sup>ice</sup>-  
bath heated to  $60^{\circ}\text{C}$  and stirred  
occasionally until all the  
oxide had dissolved. The  
excess of the tetroxalate was  
then determined by the same  
permanganate solution.

The solution was then poured  
into a liter Florence flask,



and zinc oxide added until the sulphuric acid was neutralized, and a small amount of the oxide remained in suspension, it would seem to be in advantage, since it neutralizes the sulphuric acid formed in the subsequent reaction, but a considerable excess is to be avoided, for it obscures the end-reaction. Five grams of zinc sulphate were then added and the solution heated to boiling.

Into another flask of the same size there was then drawn off from a burette the amount of permanganate necessary to precipitate the manganese,



assuming the oxide to be  $MnO_2$ ,  
as well as enough to precipitate  
the manganese derived from  
the permanganate used in  
titrating the excess of bisulphate.  
The boiling solution of manganese  
sulphate was then rapidly  
poured into this and the  
flask rinsed 3 or 4 times  
with hot water. The flask  
was then shaken 5 or 6 times  
and the precipitate allowed  
to settle. More permanganate  
was then added from the  
burette until the solution  
retains the pink color  
after shaking 10 or 12 times.  
Since the difficulty in this  
method is altogether in



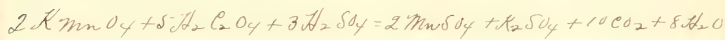
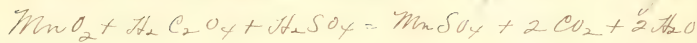
The determination of Manganese, it has been found advantageous in the latter part of the work to make up the manganous sulphate solution to 200 cc., and to determine the manganese in 50 cc portions of this, each time drawing off, to within 10 cc. the amount of permanganate required in the preceding analysis. The first analysis is generally a little low; the subsequent ones show close agreement, of course, about 4 times as much oxide must be reduced when this method is used.

The equations representing the reactions involved in the





above method are the following



Oxalic acid is written instead of potassium tetroxalate as it simplifies the equations.

Now,  $\frac{1}{2}$  molecule  $\text{MnO}_2$  contains  $\frac{2}{3}$  as much available oxygen as  $\frac{1}{2}$  molecule of  $\text{KMnO}_4$ .

$\frac{1}{2}$  molecule  $\text{MnSO}_4$  requires  $\frac{2}{3}$  mol.  $\text{KMnO}_4$  to precipitate it.

Now in an analysis the ratio of the number of molecules of permanganate <sup>which are</sup> equivalent in available oxygen to the number of molecules of  $\text{MnO}_2$  present, to the number of molecules of permanganate required



to precipitate the manganese derived from the  $MnO_2$  is  $\frac{2}{3} : \frac{2}{3}$  or 6:10, or the number of c.c. of permanganate which are equivalent to the number of c.c. of nitrosalate oxidized by the  $MnO_2$ , multiplied by  $\frac{1}{6}$  is equal to the number of c.c. of permanganate required to precipitate the manganese. Now if more than this amount is used, the oxide contains relatively more manganese than is possible, and the ratio of the number of c.c. used to the number calculated as above is the ratio of the total number of molecules of  $MnO$  to the number



of molecules of  $\text{MnO}_2$ , or, since each molecule of  $\text{MnO}_2$  contains 1 atom of available oxygen, of  $\text{MnO} : \text{C}$

Of course in an actual determination the number of cc. of permanganate used to precipitate the manganese sulphate must be corrected for the manganese introduced in titrating the excess of tetroxalate. This is done by deducting  $\frac{2}{3}$  of the number of cc. introduced, since 1 mol. <sup>oxide</sup>  $\text{KMnO}_4$  gives 1 mol.

$\text{MnSO}_4$  which requires  $\frac{2}{3}$  mol.  $\text{KMnO}_4$  to precipitate it

Remarks on the method.

It will be seen from the previous



Statements that the Volhard  
method for the determination  
of manganese has been consider-  
ably modified. In the Volhard  
method, a standardly prepared  
ferrous solution is run from a  
burette into the hot manganous  
sulphate solution which contains  
zinc sulphate, and one or two  
drops of nitric acid. The  
accuracy of this method was  
tested as follows; a certain  
number of c.c. of permanganate  
solution were exactly  
reduced by tetroxalate. It  
should require  $\frac{2}{3}$  of the number  
of c.c. reduced to precipitate  
the manganous as manganous





It was again, however, that the end reaction was obtained before this amount had been added except when very small quantities were used.

A few of the results obtained are given below.

Column I contains the calculated number of C.C. required to precipitate the manganese, i.e.,  $\frac{2}{3}$  of the number of C.C. reduced.  
Column II the number of C.C. required.

Column III, the amount of Mn. in the solution.

Column IV the amount of Mn. found.

Column V, the deficiency in per cent.



<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>
20.04	20.04	.1035	.1032	.24
30.15	30.07	.15525	.15497	.24
41.62	41.38	.21441	.21312	.60
52.30	52.84	.27451	.27214	.86

The error increases rapidly as the amount of manganese increases, but using the modified method, however, accurate results could be obtained as long as the Mn. in the solution did not exceed 15 gram. When larger quantities were used, lower results were always obtained, and the error increased with increasing quantities of manganese, just as in the other method.



although it was very much  
less. The probable reasons  
for the greater accuracy  
are the following

1. In mixing the manganous  
sulphate and permanganate  
solutions, there is an excess  
of permanganate almost  
to the end of the reaction  
thus decreasing the chances  
of formation of any oxides  
of manganese lower in  
oxygen than  $MnO_2$ .

2. The solution is kept very  
nearly neutral to the end  
of the determination. An  
excess of zinc oxide neutral-  
izing the sulphuric acid  
as soon as formed



✓ The necessity of using nitric acid is obviated by using sulphuric acid. It has been shown that  $MnO_2$  will decompose permanganate, in the presence of either sulphuric or nitric acid, quite readily at a temperature near  $100^\circ C$ .

B. Methods used for the determination of the percentage composition of oxides containing  $MnO$ ,  $K_2O$  or  $NH_3$ ,  $H_2O$  and  $O$ .

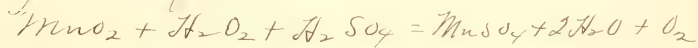
1)  $MnO$ . - This was determined by reducing about 2 grams of the oxide with sodium sulphite and sulphuric acid, evaporation of the excess of sulphur dioxide





and precipitation of the manganese by the modified Volhard method.

2) Total base, i.e.,  $MnO + K_2O$  or  $NH_3$  about 2 gram was treated with an excess of standard sulphuric acid and hydrogen peroxide and warmed until the oxide had completely dissolved. The excess of acid was then determined by titration with a solution of ammonia using litmus as the indicator. The reaction involved in the solution of the oxide is expressed by the equation:



A large excess of hydrogen peroxide should be avoided



because it impairs the  
sensitivity of the indicator,  
also because it causes a  
precipitation of oxide in  
the solution as each drop  
of ammonia is added.

This dissolves readily by  
stirring as long as the  
solution is acid, the  
precipitation can however  
be almost entirely avoided  
by using only a slight  
excess of the peroxide.

This method gives the amount  
of sulphuric acid neutralized  
by the  $MnO + K_2O + NH_3$ , that  
required for the  $MnO$  is easily  
calculated from the  
previous determination



by the Volhard method, the difference is that neutralized by the  $\text{NaOH}$  from which their percent can be easily calculated,

3. Ammonia- In addition to the above method the ammonia was determined by reducing a portion with sulphurous acid and sulphuric acid, transferring to a Kjeldahl distilling-apparatus, rendering alkaline with potassium hydroxide, and collection of the ammonia in standard sulphuric acid. The results by the two methods showed close agreement.

The silver bromide present



an impurity in a number of samples was determined in the same portion by filtering off and weighing after the oxide had dissolved. # available oxygen this was determined in a weighed portion in the same manner as directed under A.

The  $MnO$ ,  $K_2O$  ( $\approx NH_3$ ) and available  $O$ . can all be determined in the same portion, if desired, as follows: Dissolve in tetroxalate and standard sulphuric acid, titrate the excess of tetroxalate with permanganate, then add 1 or 2 drops of hydrogen peroxide to prevent precipitation of oxide, and





titrate the excess of acid by ammonia, then acidify again and destroy the hydrogen peroxide with permanganate, and determine the total manganese by the Volhard method.

Owing to the <sup>ex-ite</sup> complication of this method and the corrections to be introduced at each step, it was seldom used.

5. To determine the ratio of  $K_2O:MnO$  in the same sample.

Dissolve in standard sulphuric acid with the addition of hydrogen peroxide titrate the excess of acid with ammonia, then acidify and titrate the excess of hydrogen peroxide



with permanganate, then determine the total manganese by the volhard method, knowing the relation between the sulphuric acid and permanganate the ratio of  $K_2O : MnO$  is easily calculated.

6. Determination of water.

a. When the oxide contained ammonia.

About .5 gram was weighed out into a platinum boat and placed in a combustion tube in a short gas-furnace, weighed glass-stoppered U-tube, containing glass beads and sulphuric acid were attached to both ends of the tube, a slow current of air dried by sulphuric acid was



passed through the apparatus. The U-tubes contained just enough sulphuric acid so that the air was forced to pass through it. The oxide was then heated and the water collected in the tubes.

It was found that the result must be corrected for the amount of water formed from the ammonia. No free ammonia is given off.

This was proved by attaching a Peligot tube to the apparatus containing standard acid, and heating some oxide as before. It was found that no acid was neutralized when the oxide contained  $K_2O$ .



The method of procedure in this case was exactly the same as in the preceding, except that the oxide was mixed with lead oxide ( $PbO$ ) to facilitate the elimination of water. In some cases Chromium oxide ( $Cr_2O_3$ ) was used.

#### V Accuracy of these methods.

It is not considered possible by these methods to distinguish between two such compounds as  $MnO\ 19\ MnO_2$  and  $MnO\ 20\ MnO_2$ . It is believed, however, that  $MnO\ 19\ MnO_2$  can be distinguished from  $MnO\ 21\ MnO_2$ , but this is the limit of their accuracy. The percentage composition





of the three compounds is given below

	MnO	O <sub>2</sub>
MnO 19 MnO <sub>2</sub>	82.35	17.65
MnO 20 MnO <sub>2</sub>	82.32	17.68
MnO 21 MnO <sub>2</sub>	82.28	17.72

VI The results of analysis  
 Oxide no. 1. This was prepared June 10  
 1895 by method B. It was placed  
 in a glass dish in a desiccator  
 containing sulphuric acid,  
 it was exposed only to diffused  
 light. Analyzed Mar. 2 '96

	Found	Corrected for NH <sub>3</sub> + aq. Br	Calculated for MnO 10 MnO <sub>2</sub> + 6 aq. Br
MnO	77.27	77.77	77.68
O <sub>2</sub>	16.65	16.76	16.69
H <sub>2</sub> O	5.21	5.24	5.62
NH <sub>3</sub>	.14		
aq. Br	.56		



Oxide no 2. Prepared June 10 '95,  
It was placed in a crystallizing-  
dish in a desiccator containing  
sulphuric acid. It was exposed  
to the direct rays of the sun.

	analyzed Feb. 25 '96	corrected for N <sub>2</sub> O <sub>3</sub> + aq. H <sub>2</sub> O	calculated for MnO 20 MnO <sub>2</sub> 10 H <sub>2</sub> O
MnO	77.37	77.70	77.68
O <sub>2</sub>	16.82	16.90	16.67
H <sub>2</sub> O	5.38	5.40	5.63

This oxide was lost by an  
accident after the above three  
determinations were made. The  
calculations are made by  
determining the N<sub>2</sub>O<sub>3</sub> + aq. H<sub>2</sub>O by  
difference

Oxide no 3. This was prepared June 10,  
'95 by method B. It was placed  
in a glass dish in a desiccator



Containing phosphorus pentoxide.  
It was exposed only to diffused  
light. It was analyzed Mar 8 '96  
corrected for calculated for  
Found  $NH_3 + 12H_2O$   $MnO 20 MnO_2 + 6H_2O$

MnO	77.13	77.91	77.68
O <sub>2</sub>	16.42	16.59	16.10
H <sub>2</sub> O	5.55	5.62	5.63
NH <sub>3</sub>	2.2		
Ag <sub>2</sub> O	79		

Side note. Preserved since 11<sup>th</sup>  
by method 2. It was placed  
in a small dish in a  
desiccator containing phosphorus  
pentoxide. It was exposed  
to the direct sunlight, when  
analyzed Mar. 11 '96 the following  
results were obtained.

Found	corrected for $NH_3 + 12H_2O$	calculated for $MnO 20 MnO_2 + 4H_2O$
MnO 78.76	78.82	78.17



O <sub>2</sub>	16.85	16.99	17.01
H <sub>2</sub> O	3.58	3.61	3.83
4H <sub>2</sub>	1.1		
4H <sub>2</sub>	1.1		

This oxide had apparently lost 2 molecules more water than the preceding one. This was probably due to the fact that the latter was subjected to a much higher temperature during the summer months as it "stood" in the sunlight. Oxide nos. This oxide was prepared June 10 '96 by Method B. It was placed in a glass dish in a desiccator which contained calcium chloride. It was exposed only to diffused light; analyzed Mar 16 '96





	Found	corrected for Nb + Ta	calculated for but 1.5 substituted
MnO	75.96	76.64	76.75
O <sub>2</sub>	15.79	15.92	16.02
FeO	7.37	7.44	7.22
NH <sub>3</sub>	.21		
Ag <sub>2</sub> O	.68		

Oxide no. 6. This was prepared June 10 '45 by method B. It stood in a desiccator containing calcium chloride, in the sunlight. It was analyzed Nov. 1946

	Found	corrected for Nb + Ta	calculated for MnO 12.5 MnO <sub>2</sub> 5.2 Al
MnO	75.63	76.29	76.21
O <sub>2</sub>	15.77	15.91	15.91
FeO	7.44	7.55	7.22
NH <sub>3</sub>	.20		
Ag <sub>2</sub> O	.68		

This oxide and the preceding one, both standing over calcium



Chloride contained much less oxygen than those which stood over the more effective drying agents, a possible explanation of this is that it was due to the alternate absorption and loss of water by the sides of the Calcium Chloride has a large temperature coefficient.

Oxide no 7. This was prepared June 10 '95, by method B. It was placed in a glass crystallizing-dish in a desiccator which contained about 250 cc. of water. Although it stood in an atmosphere saturated with water vapor, it was quite dry and ready to use



This was no doubt due to the fact that it stood in the sunlight and was at times heated to a considerable extent.

It was analyzed Mar 24 '91

Found	calculated for $NH_3 + AgBr$	calculated for $MnO \cdot 15H_2O + 4\frac{1}{2}H_2O$
MnO 77.34	78.06	77.95
$O_2$ 16.34	16.49	16.48
$H_2O$ 5.52	5.57	5.56
$NH_3$ .22		
$AgBr$ .70		

Quade no 8. This oxide was prepared June 10 '95 by Method B. It was placed in a beaker, covered with about 100 cc of water and set in a desiccator. It was exposed to the sunlight. Owing to an imperfectly fitting cover, the water evaporated during



The summer months. It was analyzed April 8, '76 and gave the following results

Found	corrected for $H_2O + aq^n$	calculated for $MnO \cdot 2O$	calculated for $MnO_2 + \frac{1}{2}H_2O$
Mn 71.12	74.32	74.33	
O <sub>2</sub> 16.15	17.61	17.64	
H <sub>2</sub> O 3.24	3.27	3.36	
NH <sub>3</sub> .27			
Loss 6.9			

Oxide no 9. This oxide was prepared June 18, '76 by method B. It was placed in a crystallizing dish in a desiccator which contained about 500 cc. of water. Unlike the oxide which was placed in the sunlight, this oxide lost scarcely any water, and was still of the consistency of a thick paste





Since a complete analysis  
could not be satisfactorily  
made, of it in this condition  
only the ratio of  $MnO$  to  $O$   
was determined in it.

It was analyzed Mar 26 '96  
Ratio  $MnO : O$  found .9482

Calculated for  $MnO \cdot 18 MnO_2$  .9474

Grade no 10, Prepared June 18 '95  
by method B. It was placed  
in a beaker, covered with  
about 150 cc of water and  
enclosed in a desiccator.  
It was exposed only to diffused  
light. It was analyzed  
April 10 '96

Ratio of  $MnO : O$  found 1.9523

Calculated for  $MnO \cdot 20 MnO_2$  1.9524

This completes the series of



oxides prepared by Method B.

Those following all contained 120. Complete analyses were made of some, while in other cases only the ratio of  $MnO:O$  was determined.

Oxide no 11. This was prepared Oct 20 1894 according to method A. It was placed in a desiccator containing phosphorus pentoxide, and allowed to stand in a position exposed only to diffused light. Its composition in regards the ratio of  $MnO:$ , at different times was as follows.

Jan 4 '95, Ratio  $MnO:O$  found 1: 4854

Calculated for  $MnO \cdot 70 MnO_2$  1: 4859

Mar 27 '95 Ratio  $MnO:O$  1: 4658

calculated for  $MnO \cdot 28 MnO_2$  1: 4655



May 8 '95 ratio  $MnO:O$  1: 9646

Calculated for  $MnO \cdot 2/3 MnO_2$  1: 9643

April 15 '96, ratio  $MnO:O$  1: 9654

Calculated for  $MnO \cdot 2/3 MnO_2$  1: 9655

It will thus be seen that the composition remained practically constant from May 27 '95 to April 15 '96. A complete analysis was made on the latter date with the following results.

Found		Calculated for
		$3 MnO \cdot 2 MnO_2 \cdot 3 H_2O / H_2O$
$MnO$	71.60	71.76
$O$	15.59	15.61
$H_2O$	8.14	8.14
$H_2O$	4.58	4.49

Grade no 12. This was prepared according to method A. on Oct 20 '94



It was placed in a desiccator containing phosphorus pentoxide and exposed to the sunlight. Its composition was as follows.

Jan. 8 '95, ratio  $MnO : O$  1: 4720

Calculated for  $MnO\ 35\ MnO_2$  1: 4722

Mar 22 '95 ratio  $MnO : O$  1: 4520

Calculated for  $MnO\ 20\ MnO_2$  1: 4524

May 18 '95 ratio  $MnO : O$  1: 4522

Calculated for  $MnO\ 20\ MnO_2$  1: 4524

April 20 '96 ratio  $MnO : O$  1: 9428

Calculated for  $MnO\ 16.5\ MnO_2$  1: 9428

This oxide slowly lost oxygen until it reached the composition  $MnO\ 20\ MnO_2$ , where it remained for some time. During the following year, however, it lost still more, and finally attained





The composition  $MnO$  16.8  $MnO_2$   
 a complete analysis was made  
 April 20. '96

		Calculated for
Found		5 $MnO$ 75 $MnO_2$ 44 $H_2O$ 4 $K_2O$
$MnO$	70.35	70.54
$O$	14.96	14.92
$H_2O$	9.86	9.85
$K_2O$	4.70	4.69

oxide no 13. Prepared Oct 20 '94 by  
 method A. It was placed in  
 a desiccator containing calcium  
 chloride in a position exposed  
 to the direct sunlight. It analyzed !!  
 as follows.

Jan 9 '95 ratio  $MnO:O$  1: 9681

Calculated for  $MnO$  30  $MnO_2$  1: 9677

Mar 22 '95 ratio  $MnO:O$  1: 9521

Calculated for  $MnO$  30  $MnO_2$  1: 9524



May 16 '95 ratio  $\text{MnO}:\text{O}$  1: 9436

Calculated for  $\text{MnO} 16.5 \text{ MnO}_2$  1: 9428

April 23 '96 ratio  $\text{MnO}:\text{O}$  1: 9229

Calculated for  $\text{MnO} 12 \text{ MnO}_2$  1: 9230

A complete analysis made up of 28

76 gave the following results.

Calculated for

Found		5 MnO 58 MnO <sub>2</sub> 40 H <sub>2</sub> O 3 K <sub>2</sub> O
MnO	69.90	69.83
H <sub>2</sub> O	11.55	11.50
K <sub>2</sub> O	11.91	11.23
K <sub>2</sub> O	4.12	4.42

Oxide no 14. Prepared Oct 20 '94

by method A. It was placed in a beaker, covered with about 150 cc water and enclosed in a desiccator. It was exposed to the sunlight.

Can 10. '95 ratio  $\text{MnO}:\text{O}$  1: 9878



calculated for  $MnO \cdot 2MnO_2$  1:1.76.  
 When the next analysis came to  
 be made, it was found that  
 the water had escaped, so that  
 all the subsequent analyses  
 were made on a dry oxide.

Mar 26 '95 ratio  $MnO : O$  1: .9659

calculated for  $MnO \cdot 2MnO_2$  1: .9655

May 21 '95 ratio  $MnO : O$  1: .9635

calculated for  $MnO \cdot 2MnO_2$  1: .9630

May 5 '96 ratio  $MnO : O$  1: .9585

calculated for  $MnO \cdot 2MnO_2$  1: .9582

a complete analysis, May 76  
 gave the following results:

Calculated for

Found		2 MnO 4 MnO <sub>2</sub> 2 K <sub>2</sub> O 11 H <sub>2</sub> O	
MnO	74.92	MnO	74.21
O	18.98	O	18.92
K <sub>2</sub> O	4.75	K <sub>2</sub> O	5.01
H <sub>2</sub> O	4.35	H <sub>2</sub> O	4.81



Oxide no 15; This was prepared Oct 20. 1894, by method A. It was placed in a crystallizing dish in a desiccator which contained about 250 cc water. The oxide remained moist for some time, but, when the complete analysis was made, it was quite dry and easily powdered. Although it stood in an atmosphere saturated with water vapor. The results of the analyses were as follows.

Jan 9 '95	ratio $MnO : O$	1 : .7840
	calculated for $MnO .60 MnO_2$	1 : .7836
Mar 25 '95	ratio $MnO : O$	1 : .9596
	Calculated for $MnO .24 MnO_2$	1 : .9600
May 18 '95	ratio $MnO : O$	1 : .9562
	Calculated for $MnO .22 MnO_2$	1 : .9565





May 18 '96 ratio  $MnO : O$  1: 95.12

calculated for  $5MnO \cdot 94MnO_2$  1: 95.24

The complete analyses made May 18 '96 gave the following results.

		Calculated for	
Found		$5MnO \cdot 94MnO_2 \cdot 5K_2O \cdot 55H_2O$	
$MnO$	70.05		70.31
$O$	15.03		15.06
$K_2O$	4.77		4.72
$H_2O$	9.94		9.91

Quade no 16, This was prepared Oct 20 '94 by method A. It stood in a desiccator over sulphuric acid in diffused light. The analyses were as follows.

Jan 3 '95 ratio  $MnO : O$  1: 95.22

calculated for  $5MnO \cdot 55MnO_2$  1: 95.21

April 1 '95 ratio  $MnO : O$  1: 96.12



Calculated for  $MnO \cdot 25 MnO_2$  1: 9615  
 May 11 '95 ratio  $MnO : O$  1: 9615

Calculated for  $MnO \cdot 25 MnO_2$  1: 9615  
 Oxide no 17. Prepared Oct 20 '94 by  
 method A. This oxide was placed  
 in a desiccator over calcium  
 chloride and was exposed to  
 diffused light only. It analyzed  
 as follows.

Jan 5 '95 ratio of  $MnO : O$  1: 9835

Calculated for  $MnO \cdot 60 MnO_2$  1: 9836

Mar 29 '95 ratio of  $MnO : O$  1: 9522

Calculated for  $MnO \cdot 20 MnO_2$  1: 9524

May 13 '95 ratio of  $MnO : O$  1: 9526

Calculated for  $MnO \cdot 20 MnO_2$  1: 9524

Oxide no 18. This was prepared  
 Oct 23 '94 by method A. It was  
 spread out on a drying-  
 plate and left under a



large bell-jar. The analyses were as follows.

Jan 7 '95 ratio  $\text{MnO}:\text{O}$  1: 9904

Calculated for  $\text{MnO}_{100}\text{MnO}_2$  1: 9901

Apr 11 '95 ratio  $\text{MnO}:\text{O}$  1: 9718

Calculated for  $\text{MnO}_{100}\text{MnO}_2$  1: 9722

May 23 '95 ratio  $\text{MnO}:\text{O}$  1: 9689

Calculated for  $\text{MnO}_{100}\text{MnO}_2$  1: 9687

Grade no 11. This was prepared Oct 20 '94 by method A. It was placed in a beaker, covered with about 150 cc. water, and enclosed in a desiccator. It stood in diffused light. The analyses were as follows.

Jan 7 '95 ratio  $\text{MnO}:\text{O}$  1: 9905

Calculated for  $\text{MnO}_{100}\text{MnO}_2$  1: 9901

April 3 '95 ratio  $\text{MnO}:\text{O}$  1: 9760

Calculated for  $\text{MnO}_{100}\text{MnO}_2$  1: 9756



May 14 '95 ratio  $\text{MnO}:\text{O}$  1: 9690  
 calculated for  $\text{MnO} 31 \text{ MnO}_2$  1: 9687

May 8 '96 ratio  $\text{MnO}:\text{O}$  1: 9672  
 calculated for  $\text{MnO} 30 \text{ MnO}_2$  1: 9677

Oxide no 20. This was prepared  
 Oct 20 '94 by method A. It stood  
 in a desiccator over water, in  
 diffused light. Its analyses  
 were as follows.

Jan 7 '95 ratio of  $\text{MnO}:\text{O}$  1: 9948  
 calculated for  $\text{MnO} 200 \text{ MnO}_2$  1: 9950

April 2 '95 ratio  $\text{MnO}:\text{O}$  1: 9679  
 calculated for  $\text{MnO} 50 \text{ MnO}_2$  1: 9677

May 10 '95 ratio  $\text{MnO}:\text{O}$  1: 9670  
 calculated for  $\text{MnO} 24 \text{ MnO}_2$  1: 9667

May 9 '96 ratio  $\text{MnO}:\text{O}$  1: 9460  
 calculated for  $\text{MnO} 17.5 \text{ MnO}_2$  1: 9459

Oxide no 21. This was prepared  
 Oct 22 '94 by method A. It stood





from that time until Jan 18 '96  
under a bell jar, when it  
was placed on a watch-  
glass in a desiccator which  
contained a strong alkaline  
solution of pyrogallol. It  
was analyzed Jan 7 '95, and  
the ratio of  $MnO$  to  $O$  corresponded  
to the formula  $MnO_{100}MnO_2$ .  
The subsequent analyses were  
as follows.

Mar 28 '95 ratio of  $MnO:O$  1: 9655

Calculated for  $MnO_{28}MnO_2$  1: 9655

May 12 '95 ratio  $MnO:O$  1: 9642

Calculated for  $MnO_{27}MnO_2$  1: 9643

Jan 24 '96 ratio  $MnO:O$  1: 9559

Calculated for  $MnO_{22}MnO_2$  1: 9565

Grade no 22. This was prepared  
Oct 23 '94 by method A. It stood



from that time until Jan 20  
 '95 on a drying-plate, at  
 that time it was placed in a  
 beaker and about 100 cc  
 of 2-Normal nitric acid poured  
 over it. It was then placed  
 under a bell-jar, and  
 was exposed to diffused light  
 only. The ratio of the  $MnO : O$   
 was determined a few days  
 before it was placed under  
 the nitric acid, and found  
 to correspond to the formula  
 $MnO 100 MnO_2$ . The ratio of  
 the  $MnO : O$  and of the  $K_2O : MnO$   
 was determined May 12 '96  
 the results were

Ratio  $MnO : O$  1: 9622

Calculated for  $MnO 25 MnO_2$  1: 9615



Ratio of  $K_2O$ :  $MnO$  1:46

The solution was found to contain considerable manganese.

Oxide no 23, This was another portion of the same oxide as no 22. It was placed under 2-N. nitric acid at the same time. The results of analysis were as follows

May 12 '96, ratio  $MnO$ : $K_2O$  1:95.27

Calculated for  $Mn_2O_3$ : $K_2O$  1:95.24

Ratio of  $K_2O$ :  $MnO$  1:40

There was also found to be considerable manganese in solution.

Oxide no 24, This was a third portion of the same oxide which was placed under



4N. nitric acid. The other conditions were the same. The results of the analyses were

Mass ratio  $MnO_2$  1: 98.91  
 Calculated for  $MnO_2 \cdot 4H_2O$  1: 96.00  
 Ratio of  $K_2O$ :  $MnO$  1: 46.

### Conclusions

- 1 There is a considerable error in the Volhard method for the determination of Manganese which can largely be avoided by a slightly different method of procedure.
- 2 In the decomposition of  $MnO_2$  prepared by wet methods there is a strong tendency to form compounds





of the general formula  $MnO_{2.5}x(MnO_2)$  especially those which lie between  $MnO_{10}MnO_2$  and  $MnO_{30}MnO_2$ . The compound  $MnO_{20}MnO_2$  seems to be "formed most often."

3. The composition of the compound precipitated when  $MnSO_4$  is treated with  $xMnO_2$  in the presence of 4 molecules of nitric acid to 1 of  $KMnO_4$  is probably  $K_2O_{20}MnO_{20} + xH_2O$ , since in all the analyses in which  $K_2O$  was determined the ratio of  $K_2O$  to  $MnO$  was nearly 1 to 20.

4. Nearly one-half of the  $K_2O$  in such oxides is lost by standing in air.



## Biographical.

The author was born near Woodstock Ontario May 4 1870. His early education was received at the public schools in that vicinity. In 1886 he entered Woodstock College where he spent four years. In 1888 he entered Toronto University and received the degree of B.A. in 1892. Since that time he has been pursuing his studies in the Johns Hopkins University. He was assistant to Prof. Morse for the year '94-'95 and Fellow in '95-'96.











































